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EFFECTIVE CORE POTENTIALS

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After a brief review of relativistic effects on the electronic structure of atoms and molecules the basic ideas of the relativistic ab initio effective core potential method are outlined. The underlying approximations as well as the differences between the two commonly used versions of the approach, i.e., model potentials and pseudopotentials, are discussed. The article then focusses on the adjustment of atomic shape-consistent and energy-consistent pseudopotentials, as well as on corresponding core polarization potentials. Finally, the results of some calibration calculations for the homonuclear dimers of the halogen atoms are presented.

1 Introduction

The present manuscript discusses the two branches of effective core potential (ECP) approaches, i.e., the model potential (MP) and the pseudopotential (PP) techniques. The main focus is on those ECP schemes which proved to be successful in atomic and molecular relativistic electronic structure calculations during the past decade, and moreover, due to the authors own history, the presentation is somewhat biased towards the discussion of energy-consistent ab initio pseudopotentials. It is neither intended to give a complete overview over all effective core potential approaches developed since the pioneering work of Hellmann and Gombas around 1935, nor to cover all schemes currently on the market. In particular techniques developed especially for density functional theory and/or plane wave based computational approaches have been left out. A number of reviews on effective core potentials has been published during the last three decades and the reader is referred to them for more detailed information [1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20].

1.1 Relativistic effects

Accurate ab initio electronic structure calculations for systems with heavy elements require the inclusion of relativistic effects, cf., e.g., the extensive bibliographies of relativistic calculations collected by Pyykkö [21,22,23]. Although this fact is nowadays generally acknowledged and the discussion of relativistic effects begins to be included in (quantum) chemical textbooks, a very brief and incomplete outline of relativistic effects will be given here in order to make more plausible why even for systems with second row elements a relativistic effective core potential study may be more accurate than a nonrelativistic all-electron investigation. Several excellent review articles focussing on relativistic effects exist [24,25,26,27,28,29,30,31,32,33,34,35,36,37,38].

For hydrogen and hydrogen-like ions with a point nucleus of charge Z the rela-

tivistic Schrödinger equation, i.e., the Dirac equation, is analytically solvable:

$$E_{n\kappa} = \pm c^2[1 + \left(\frac{Z/c}{n - |\kappa| + \sqrt{\kappa^2 - (Z/c)^2}}\right)^2]^{-1/2} - c^2 \ . \qquad (1)$$

Here c denotes the velocity of light (c $\approx$ 137.0359895 a.u.). The relativistic quantum number κ is defined in terms of the quantum numbers of orbital and total angular momentum, l and j, as

$$\kappa = \mp(j + 1/2) \qquad \text{for} \qquad j = l \pm 1/2 \ . \qquad (2)$$

It is observed that in contrast to the nonrelativistic case two sets of solutions exist, which are separated by $\approx 2c^2$. This is due to the fact that the Dirac equation is not only a wave equation valid for an electron, but rather for spin-1/2 particles as electrons and positrons. The solutions near the zero of energy are called electronic states and essentially correspond to the nonrelativistic solutions, whereas those near $-2c^2$ are called positronic states. The wavefunction turns out to be a four-component vector (four-spinor), the two upper components (upper bispinor) being large for the electronic states, the two lower ones (lower bispinor) being large for the positronic states (charge degrees of freedom in the wavefunction). Since the focus in relativistic quantum chemistry is on electrons, it is common to use the terms *large components* and *small components* for the upper and lower components, respectively. The odd and even components may be related to spin up and down, respectively, of the particle (spin degrees of freedom). A Taylor expansion of Eq. 1 shows for the electronic states that the nonrelativistic energy increases as Z^2 and the relativistic corrections to it as Z^4. However, since the prefactor of the relativistic energy contributions contains $1/c^2$ the corrections are expected to become chemically important only for heavy nuclei. The substitution of the nonrelativistic Hamiltonian by a relativistic one leads to the so-called *direct relativistic effects*, i.e., a stabilization and a contraction of the hydrogenic functions. It is further observed that not all states with the same main quantum number n are degenerate as it is the case for the nonrelativistic solutions. In particular, states with the same nl are split into two subsets for $l\rangle 0$ (spin-orbit splitting).

The total nonrelativistic Hartree-Fock energy of the rare gas atoms He, Ne, Ar, Kr, Xe and Rn is approximately proportional to $Z^{2.37}$, the correlation corrections (as estimated from local density functional calculations including a self-interaction correction) to $Z^{1.16}$ and the relativistic corrections (as estimated from quasirelativistic Wood-Boring calculations) to $Z^{4.34}$ (Fig. 1). Focussing on the one-electron functions rather than the total energy one observes a stabilization and contraction for valence s and p shells, but a destabilization and expansion for valence d and f shells (Figs. 2, 3). Besides the direct relativistic effects causing the stabilization and contraction as well as the splitting of the p, d, f, ... shells, so-called *indirect relativistic effects* or relativistic self-consistent field effects are present. The contraction of the inner shells causes a more efficient screening of the nuclear charge for the outer shells, thus leading to a decreased effective nuclear charge and an expansion and destabilization. Direct and indirect effects act on all shells, but direct effects dominate for s and p valence shells, whereas indirect effects dominate for d and f valence shells. Relativistic effects on orbitals have direct consequences

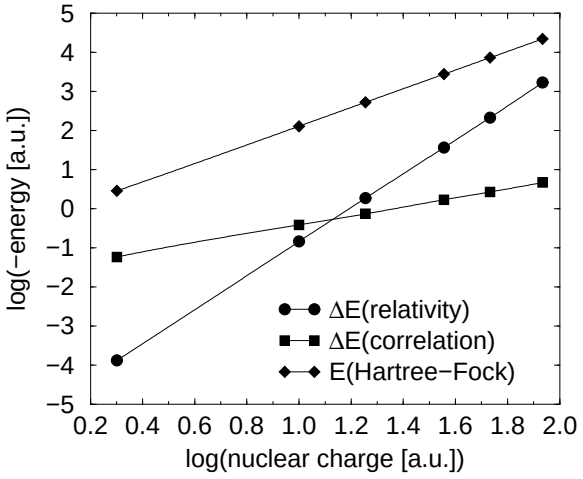

Figure 1. Total nonrelativistic Hartree-Fock energy, relativistic corrections (estimated from Wood-Boring calculations) and correlation contributions (estimated from correlation energy density functional calculations) for rare gas atoms.

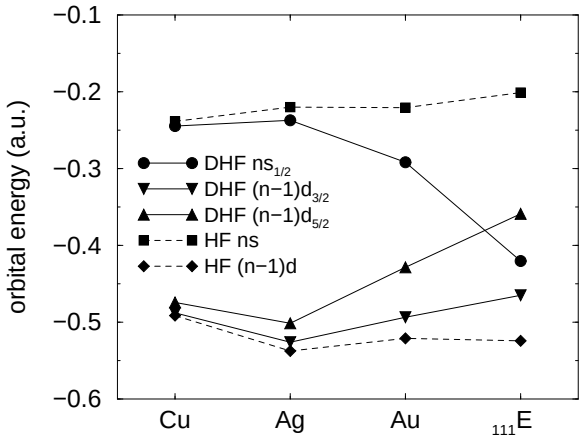

Figure 2. Nonrelativistic Hartree-Fock (HF) and relativistic Dirac-Hartree-Fock (DHF) orbital energies for the valence shells of the coinage metals (n = 4, 5, 6, 7 for Cu, Ag, Au and Eka-Au, respectively).

on quantum mechanical observables, e.g., the ionization potentials of the coinage metals are enhanced due to the relativistic stabilization of the valence s shell (Fig. 4). Clearly, since the energy and shape of valence orbitals is affected by relativistic effects, these are also important for chemical bonding. Quite often relativity leads to a bond length contraction, e.g., for the coinage metal hydrides (Fig. 5). In some rare cases, e.g., for some lanthanide or actinide systems [36], slight bond

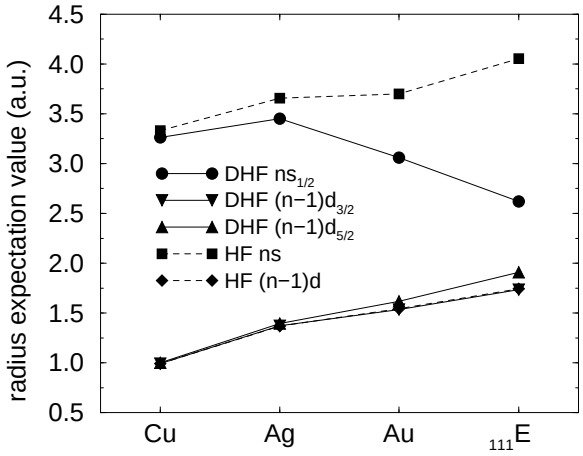

Figure 3. Nonrelativistic Hartree-Fock (HF) and relativistic Dirac-Hartree-Fock (DHF) orbital radius expectation values $\langle r \rangle$ for the valence shells of the coinage metals (n = 4, 5, 6, 7 for Cu, Ag, Au and Eka-Au, respectively.

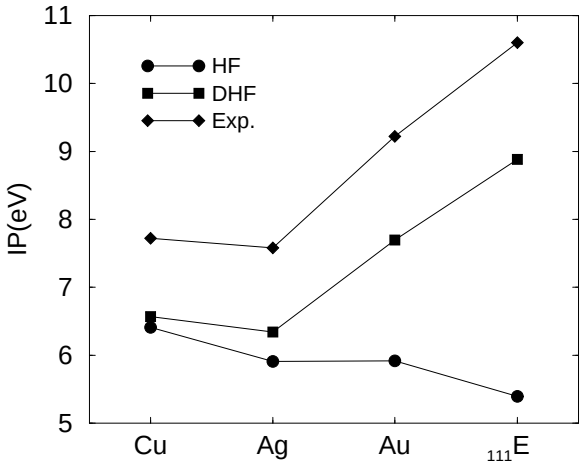

Figure 4. Nonrelativistic Hartree-Fock (HF), relativistic Dirac-Hartree-Fock (DHF) and experimental (Exp.) ionization potentials of the coinage metals. The experimental result for Eka-Au actually corresponds to the result of a high level correlated relativistic calculation (Eliav *et al.*, Phys. Rev. Lett. **73**, 3203 (1994)).

length expansions are found. One may relate the relativistic bond length changes to contractions or expansions of the valence orbitals mainly involved in bonding, but alternative explanations are also valid [27,33]. Besides bond lengths also binding energies and vibrational constants are influenced by relativistic effects. In simple cases bond stabilization or destabilization may be estimated on the basis of atomic data, e.g., for a mainly ionic A^+B^- system the relativistic effects in the ionization

potential of A and the electron affinity of B roughly determine the relativistic effect on the binding energy. Spin-orbit coupling lowers the energy of atoms with open p, d, and/or f shells. In molecules the lowering of the energy is typically much smaller due to the usually smaller number of unpaired electrons and the lower symmetry of the system. This often leads to a net destabilization of the bond by spin-orbit effects. In special cases, e.g., for the essentially van der Waals bonded dimer Hg_2, spin-orbit effects can also increase the binding energy [39].

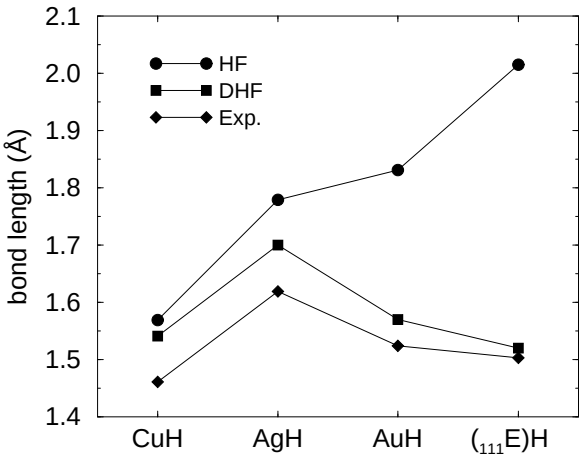

Figure 5. Nonrelativistic Hartree-Fock (HF), relativistic Dirac-Hartree-Fock (DHF) and experimental (Exp.) bond lengths of the coinage metal hydrides. The experimental result for the Eka-Au hydride actually corresponds to the result of a high level correlated relativistic calculation (Seth *et al.*, Chem. Phys. Lett. **250**, 461 (1996)).

1.2 Computational savings

More familiar than relativistic effects is to the general chemist the idea that only the valence electrons of an atom determine, at least qualitatively, its chemical behavior. The effective core potential approach is based on this experience and tries to provide a valence-only Hamiltonian which models in actual calculations for valence properties of atoms and molecules as accurately as possible the corresponding all-electron results. The main motivation to develop such schemes was initially the reduction of the computational effort, when only the chemically relevant subset of electrons is treated explicitly. Today, with a far advanced computer technology at hand and significantly improved algorithms implemented in quantum chemical program packages, the main advantage of effective core potentials is the ease with which relativistic effects can be included in the calculations.

2 All-electron Hamiltonian

Relativistic all-electron approaches are discussed here in brief for two reasons: on one hand relativistic ab initio effective core potentials are derived from (atomic) all-electron relativistic calculations, on the other hand they are often calibrated in atomic and molecular calculations against the results from all-electron relativistic calculations.

Starting point of the following considerations is a general configuration space Hamiltonian for n electrons and N nuclei, where we assume the Born-Oppenheimer approximation to hold and neglect external fields.

$$\mathcal{H} = \sum_{i}^{n} h(i) + \sum_{i\langle j}^{n} g(i,j) + \sum_{\lambda\langle\mu}^{N} \frac{Z_\lambda Z_\mu}{r_{\lambda\mu}} \ . \tag{3}$$

The indices i and j denote electrons, λ and μ nuclei. Z_λ is the charge of the nucleus λ. For the one- and two-particle operators h and g various expressions can be inserted (e.g., relativistic, quasirelativistic or nonrelativistic; all-electron or valence-only). The basic goal of quantum chemical methods is usually the approximate solution of the time-independent Schrödinger equation for a specific Hamiltonian, the system being in the state I, i.e.,

$$\mathcal{H}\Psi_I = E_I \Psi_I \ . \tag{4}$$

The most accurate electronic structure calculations nowadays applicable for atoms, molecules and also solids are based on the Dirac (D) one-particle Hamiltonian

$$h_D(i) = c\vec{\boldsymbol{\alpha}}_i \vec{p}_i + (\boldsymbol{\beta}_i - \mathbf{I}_4)c^2 + \sum_\lambda V_\lambda(r_{i\lambda}) \ , \tag{5}$$

which is correct to all orders of the fine-structure constant $\alpha = 1/c$. In these equations $\mathbf{I}_4$ denotes the 4×4 unit matrix, and $\vec{p}_i = -i\vec{\nabla}_i$ is the momentum operator for the i-th electron. $\vec{\boldsymbol{\alpha}}_i$ is a three-component vector whose elements together with $\boldsymbol{\beta}_i$ are the 4×4 Dirac matrices

$$\boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & 0 \\ 0 & -\mathbf{I}_2 \end{pmatrix} \qquad \text{and} \qquad \vec{\boldsymbol{\alpha}} = \begin{pmatrix} \vec{0} & \vec{\boldsymbol{\sigma}} \\ \vec{\boldsymbol{\sigma}} & \vec{0} \end{pmatrix} \ , \tag{6}$$

which can be expressed in terms of the three-component vector of the 2×2 Pauli matrices $\vec{\boldsymbol{\sigma}}$,

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \ , \qquad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \ , \qquad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ , \tag{7}$$

and the 2×2 unit matrix $\mathbf{I}_2$. The rest energy c^2 of the electron was subtracted from Eq. 5 in order to achieve a better compatibility to the nonrelativistic case, i.e., as in Eq. 1 the zero of energy corresponds to a free electron without kinetic energy. $V_\lambda(r_{i\lambda})$ denotes the electrostatic potential generated by the λ-th nucleus at the position of the i-th electron

$$V_\lambda(r_{i\lambda}) = -\frac{Z_\lambda}{r_{i\lambda}} \ . \tag{8}$$

In some cases a finite nucleus is used, e.g., a Gaussian-type charge distribution

$$\rho_\lambda(r) = \rho_\lambda^0 \; exp(-\eta_\lambda r^2) \qquad \text{with} \qquad 4\pi \int_0^\infty dr \; r^2 \rho_\lambda(r) = Z_\lambda \; . \tag{9}$$

The parameter η_λ can be determined from the nuclear radius R_λ, which is itself derived from the nuclear mass according to

$$\eta_\lambda = 3/(2R_\lambda^2) \qquad \text{with} \qquad R_\lambda = 2.2677 \times 10^{-5} M_\lambda^{1/3} a_0 \; . \tag{10}$$

Other charge distributions, e.g., a finite hard sphere or a Fermi-type nuclear model, are also used. The coupling of the upper and lower components of the wavefunction via $\vec{\boldsymbol{\alpha}}_i \vec{p}_i$ requires either kinetically balanced basis sets or the imposal of appropriate boundary conditions in order to avoid the so-called *finite basis set disease*.

The two-particle terms used in such calculations are either the nonrelativistic electrostatic Coulomb (C) interaction (yielding the Dirac-Coulomb (DC) Hamiltonian correct to $\mathrm{O}(\alpha^0)$)

$$g_C(i,j) = \frac{1}{r_{ij}} \; , \tag{11}$$

or in addition the magnetic Gaunt (G) interaction (yielding the Dirac-Coulomb-Gaunt (DCG) Hamiltonian correct to $\mathrm{O}(\alpha^0)$)

$$g_{CG}(i,j) = \frac{1}{r_{ij}} - \frac{\vec{\boldsymbol{\alpha}}_i \vec{\boldsymbol{\alpha}}_j}{r_{ij}} \; , \tag{12}$$

or in addition the retardation of the interaction due to the finite velocity of light, as it is accounted for in the frequency-independent Breit (B) interaction (yielding the Dirac-Coulomb-Breit (DCB) Hamiltonian correct to $\mathrm{O}(\alpha^2)$)

$$g_{CB}(i,j) = \frac{1}{r_{ij}} - \frac{1}{2r_{ij}} [\vec{\boldsymbol{\alpha}}_i \vec{\boldsymbol{\alpha}}_j + \frac{(\vec{\boldsymbol{\alpha}}_i \vec{r}_{ij})(\vec{\boldsymbol{\alpha}}_j \vec{r}_{ij})}{r_{ij}^2}] \; . \tag{13}$$

For further details the reader is referred to, e.g., a review article by Kutzelnigg [28]. The Gaunt- and Breit-interaction is often not treated variationally but rather by first-order perturbation theory after a variational treatment of the Dirac-Coulomb-Hamiltonian. The contribution of higher-order corrections such as the vaccuum polarization or self-energy of the electron can be derived from quantum electrodynamics (QED), but are usually neglected due to their negligible impact on chemical properties.

In principle problems of relativistic electronic structure calculations arise from the fact that the Dirac-Hamiltonian is not bounded from below and an energy-variation without additional precautions could lead to a *variational collapse* of the desired electronic solution into the positronic states. In addition, at the many-electron level an infinite number of unbound states with one electron in the positive and one in the negative continuuum are degenerate with the desired bound solution. A mixing-in of these unphysical states is possible without changing the energy and might lead to the so-called *continuum dissolution* or Brown-Ravenhall disease. Both problems are avoided if the Hamiltonian is, at least formally, projected onto the electronic states by means of suitable operators $\mathcal{P}_+$ (no-pair Hamiltonian):

$$\mathcal{H}_{np} = \mathcal{P}_+ \mathcal{H} \mathcal{P}_+ \; . \tag{14}$$

The Douglas-Kroll transformation [40] of the Dirac-Coulomb Hamiltonian in its implementation by Heß [41,42,43,44,45] leads to one of the currently most successful and popular forms of a relativistic no-pair Hamiltonian. The one-electron terms of the Douglas-Kroll-Heß (DKH) Hamiltonian have the form

$$h_{DKH}(i) = E_i - A_i[V(i) + \mathbf{R}_i V(i)\mathbf{R}_i]A_i - W_1(i)E_i W_1(i) - \frac{1}{2}\{W_1(i)^2, E_i\} \quad (15)$$

$$\text{with} \qquad E_i = E_{p_i} = c\sqrt{\vec{p}_i{}^2 + c^2}\ , \quad A_i = A_{p_i} = \sqrt{\frac{E_i + c^2}{2E_i}}\ , \quad \mathbf{R}_i = \frac{c\vec{\boldsymbol{\sigma}}_i\vec{p}_i}{E_i + c^2}\ ,$$

and $\{\}$ denoting an anticommutator. $W_1(i)$ is an integral operator with the kernel

$$W_1(\vec{p}, \vec{p}\,') = A_p(\mathbf{R}_p - \mathbf{R}_{p'})A_{p'}\frac{V(\vec{p}, \vec{p}\,')}{E_p + E_{p'}}\ , \quad (16)$$

where $V(\vec{p}, \vec{p}\,')$ is the Fourier transform of the external Potential $V(i)$. The two-electron terms

$$g_{DKH}(i,j) = A_i A_j[\frac{1}{r_{ij}} + \mathbf{R}_i\frac{1}{r_{ij}}\mathbf{R}_i + \mathbf{R}_j\frac{1}{r_{ij}}\mathbf{R}_j + \mathbf{R}_i\mathbf{R}_j\frac{1}{r_{ij}}\mathbf{R}_i\mathbf{R}_j]A_i A_j \quad (17)$$

increase the computational cost significantly, but have only small effects on the results and are therefore usually neglected, i.e., the unmodified Coulomb interaction is used.

A straightforward elimination of the small components from the Dirac equation leads to the two-component Wood-Boring (WB) equation [46], which exactly yields the (electronic) eigenvalues of the Dirac Hamiltonian upon iterating the energy-dependent Hamiltonian

$$h_{WB}(i) = \frac{1}{2}(\vec{\boldsymbol{\sigma}}_i\vec{p}_i)(1 + \frac{E_i - V(i)}{2c^2})^{-1}(\vec{\boldsymbol{\sigma}}_i\vec{p}_i) + \sum_\lambda V_\lambda(r_{i\lambda})\ . \quad (18)$$

Due to the energy-dependence of the Hamiltonian the Wood-Boring approach leads to nonorthogonal orbitals and has been mainly used in atomic finite difference calculations as an alternative to the more involved Dirac-Hartree-Fock calculations. The relation

$$(\vec{\boldsymbol{\sigma}}_j\vec{p}_j)f(r_j)(\vec{\boldsymbol{\sigma}}_j\vec{p}_j) = \vec{p}_j f(r_j)\vec{p}_j + i\vec{\boldsymbol{\sigma}}_j[(\vec{p}_j f(r_j)) \times \vec{p}_j] \quad (19)$$

allows the partitioning of spin-independent and spin-dependent parts and therefore the derivation of a scalar-relativistic DKH or WB Hamiltonian. This is also obtained by formally replacing $\vec{\boldsymbol{\sigma}}_i\vec{p}_i$ by $\vec{p}_i$ in Eqs. 15 and 18.

The WB approach was used to generate both model potentials as well as pseudopotentials. The DKH method was applied together with model potentials and to provide molecular all-electron results for calibration studies with valence-only schemes (cf. below).

3 Valence-only Hamiltonian

A significant reduction of the computational effort in quantum chemical investigations can be achieved by restriction of the actual calculations to the valence electron system and the implicit inclusion of the influence of the chemically inert atomic cores by means of suitable parametrized effective (core) potentials. This approach is in line with the chemists view that mainly the valence electrons of an element determine its chemical behavior, cf., e.g., the periodic table of elements. From a quantum mechanical point of view the partitioning of a many-electron system into subsystems is not possible, since electrons as elementary particles are indistinguishable. However, in the framework of effective one-particle approximations like Hartree-Fock or Dirac-Hartree-Fock theory a definition of core and valence orbitals/shells is possible either on the basis of energetic (orbital energies) or spatial (shape, radial maxima or expectation values of orbitals) arguments. If the core shells of a system are determined for one bonding situation, e.g., the free atoms, and then transferred to other bonding situations, e.g., the molecule, one speeks of the frozen-core or frozen-orbital approximation. This approach is underlying all valence-only schemes (cf., however, section 6). It is important to realize, however, that the chemists qualitative view of partitioning core and valence shells is usually not suitable for quantitative calculations, e.g., treatment of Ti ($[_{18}\mathrm{Ar}]\ 3d^2\ 4s^2\ ^3F_2$ ground state) or Ce ($[_{54}\mathrm{Xe}]\ 4f^1\ 5d^1\ 6s^2\ ^1G_4$ ground state) as a four valence electron systems leads to poor or even disastrous results [36], whereas it works very well for C ($[_2\mathrm{He}]\ 2s^2\ 2p^2\ ^3P_0$ ground state). The reason is the presence of partially occupied valence shells which have the same or even lower main quantum number as the fully occupied core shells. Although based on orbital energies the separation between core and valence shell may be reasonable, it is poor from a spatial point of view: the Ti 3d shell has its maximum density close to the one of the 3s and 3p shells, the Ce 4f shell has its maximum density even closer to the nucleus than the 5s and 5p shells. A change in the valence electron configuration in these compact valence orbitals, e.g., when looking at an excited atomic state or when forming a chemical bond, leads to too large changes of the shielding of the nuclear charge for the most diffuse core orbitals and consequently to a breakdown of the frozen core approximation. The most reliable effective core potentials have a separation of core and valence shells according to the main quantum number, e.g., 3s and 3p for Ti and 4s, 4p, 4d, 5s and 5p for Ce have to be included in the valence shell.

In effective core potential theory an effective model Hamiltonian approximation for $\mathcal{H}_{np}$ is seeked, which only acts on the states formed by the valence electrons:

$$\mathcal{H}_v = \sum_i^{n_v} h_v(i) + \sum_{i\langle j}^{n_v} g_v(i,j) + V_{cc} + V_{cpp}\ . \tag{20}$$

The subscripts c and v denote core and valence, respectively. h_v and g_v stand for effective one- and two-electron operators, V_{cc} represents the repulsion between all cores and nuclei of the system, and V_{cpp} is a core polarization potential (CPP). n_v

denotes the number of valence electrons treated explicitly in the calculations

$$n_v = n - \sum_{\lambda}^{N} (Z_\lambda - Q_\lambda) \ . \tag{21}$$

Here Q_λ denotes the charge of the core λ. Several choices exist for the formulation of such a valence-only model Hamiltonian, i.e., four-, two- or one-component approaches and explicit or implicit treatment of relativity. Since a reasonable compromise between accuracy and efficiency is desired, the standard effective core potential schemes use the implicit treatment of relativity (i.e., a nonrelativistic kinetic energy operator and inclusion of relativistic effects via parametrization of the effective core potential) and a one-component (scalar-quasirelativistic) or a two-component (quasirelativistic) treatment. Moreover, one may decide to keep the radial nodal structure of the (atomic) valence orbitals unchanged (model potentials, MP), or formally apply a pseudoorbital transformation to have the energetically lowest (atomic) valence orbital of each lj or l quantum number without radial nodes (pseudopotentials, PP).

Scalar-quasirelativistic and quasirelativistic effective core potentials use a formally nonrelativistic model Hamiltonian

$$h_v(i) = -\frac{1}{2}\Delta_i + V_{cv}(i) \qquad \text{and} \qquad g_v(i,j) = \frac{1}{r_{ij}} \qquad . \tag{22}$$

Relativistic contributions result only from the parametrization of the effective core potential V_{cv}, which describes the interaction of a valence electron with all nuclei and cores present in the system. The molecular pseudopotential is assumed to be a superposition of atomic pseudopotentials, with the Coulomb attraction between point charges as the leading term

$$V_{cv}(i) = \sum_{\lambda}^{N} (-\frac{Q_\lambda}{r_{\lambda i}} + \Delta V_{cv}^{\lambda}(\vec{r}_{\lambda i})) + ... \qquad . \tag{23}$$

For the interaction between nuclei and cores the point charge approximation also is the first term

$$V_{cc} = \sum_{\lambda\langle\mu}^{N} (\frac{Q_\lambda Q_\mu}{r_{\lambda\mu}} + \Delta V_{cc}^{\lambda\mu}(r_{\lambda\mu})) + ... \qquad . \tag{24}$$

It is hoped that a suitable parametrization of ΔV_{cv}^{λ} and $\Delta V_{cc}^{\lambda\mu}$ is able to compensate for all errors resulting from the simplifications of the original valence Hamiltonian.

3.1 Model Potentials

The most straightforward approach to come to an effective core potential is to use the Fock operator $\mathcal{F}_v$ of a valence orbital φ_a^V and to simplify the effective one particle potential

$$-\sum_{\lambda}^{N} \frac{Z_\lambda}{r_{\lambda i}} + \sum_{c} (2J_c(i) - K_c(i)) = \sum_{\lambda}^{N} (-\frac{Q_\lambda}{r_{\lambda i}} + \Delta V_{cv}^{\lambda}(\vec{r}_{\lambda i})) \ , \tag{25}$$

where the first sum is over all nuclei λ with charge Z_λ and the second over all core orbitals c. J_c and K_c denote the usual Coulomb and exchange operators. A first approximation is the assumption of non-overlapping cores, so that the second sum on the lhs can also be regarded as a superposition of one-center terms. A second approximation follows from the goal that relativistic effects should be treated implicitly. Therefore not only V_{cv} is approximated but also an additive relativistic correction term V_{rel}. In order to obtain the relevant atomic potentials $V^\lambda_{rel} + V^\lambda_{cv}$ a two- or one-component quasirelativistic atomic all-electron calculation is performed. The most widely used variant of the method are the ab initio model potentials (AIMP) of Seijo, Barandiarán and coworkers [48,49,50,51,52,53], where the quasirelativistic Hamiltonian proposed by Wood and Boring (WB) [46] for density functional calculations is used in the framework of Hartree-Fock theory according to the scheme outlined by Cowan and Griffin (CG) [47]. The WB and CG approaches correspond essentially to the use of an energy-dependent one-particle Hamiltonian, which results from the elimination of the small components from the Dirac-equation, within the Hartree-Fock scheme, disregarding any resulting non-orthogonality between orbitals of equal lj.

The AIMP method in its present form starts from a quasirelativistic all-electron Hartree-Fock calculation for the atom under consideration in a suitable electronic state and approximates the operators on the lhs of Eq. 25 for an atomic core λ as described in the following.

The long-range local Coulombic (C) part is spherical and is represented by a linear combination of Gaussians with prefactors $1/r$, i.e., a local radial model potential

$$-\frac{Z_\lambda - Q_\lambda}{r_{\lambda i}} + 2\sum_{c\in\lambda} J^\lambda_c(i) = \frac{1}{r_{\lambda i}} \sum_k C^\lambda_k e^{-\alpha^\lambda_k r^2_{\lambda i}} = \Delta V^\lambda_C(i) \ . \tag{26}$$

The exponents α^λ_k and coefficients C^λ_k are adjusted to the all-electron potential in a least-squares sense under the constraint that $\sum_k C^\lambda_k = Z_\lambda - Q_\lambda$ in order to enforce the correct asymptotic behavior of the model potential. Since the evaluation of integrals over such a local potential is not costly, any desired accuracy can be easily achieved by using a sufficiently long expansion. The nonlocal exchange (X) part is substituted by its spectral representation in the space defined by a set of functions χ^λ_p centered on core λ

$$-\sum_{c\in\lambda} K^\lambda_c(i) = \sum_{p,q} |\chi^\lambda_p(i)\rangle A^\lambda_{pq} \langle\chi^\lambda_q(i)| = \Delta V^\lambda_X(i) \ . \tag{27}$$

It should be noted that this model potential operator yields the same one-center integrals as the true core exchange operator as long as the basis functions can be represented by the set of the χ^λ_p. Two- and three-center integrals are approximated. Since, in contrast to the Coulomb part, the exchange part is short ranged, a moderate number of functions χ^λ_p is needed and the one-center approximation is expected to be very good, at least for not too large cores. In practical applications the basis used in the spectral representation is chosen to be identical to the primitive functions of the valence basis set used for the atom under consideration and the A^λ_{pq} are calculated during the input processing of each AIMP calculation.

With the Coulomb and exchange parts of the model potential discussed so far the core-like solutions of the valence Fock equation still would fall below the desired valence-like solutions. In order to prevent the valence-orbitals to collapse into the core during a variational treatment and to retain a Aufbau principle for the valence electron system, the core-orbitals are shifted to higher energies by means of a shift operator

$$P^{\lambda}(i) = \sum_{c\in\lambda} (D_c^{\lambda}) |\varphi_c^{\lambda}(i)\rangle\langle\varphi_c^{\lambda}(i)| \ . \tag{28}$$

Here the φ_c^{λ} denote the core orbitals localized on core λ. For practical calculations they are represented by a sufficiently large (all-electron) basis set. In principle only $D_c^{\lambda} \to \infty$ would effect a strict orthogonality between core and valence orbitals, however the more or less arbitrary choice $D_c^{\lambda} = -2\epsilon_c^{\lambda}$ is usually made due to numerical reasons. With this choice there is not strict orthogonality between core and valence orbitals, but the resulting errors are expected to be small.

The approach which has been described so far is the nonrelativistic AIMP method. It should be noted that for the derivation of the model potential

$$\Delta V_{cv,av}^{\lambda}(i) = \Delta V_C^{\lambda}(i) + \Delta V_X^{\lambda}(i) + P^{\lambda}(i) \tag{29}$$

no valence properties, e.g., valence orbitals or valence orbital energies, have been used in the nonrelativistic AIMP approach. The scalar-quasirelativistic and quasirelativistic extensions of the AIMP approach are called CG-AIMP (one-component) and WB-AIMP (two-component), respectively.

For an one-electron atom in the central field approximation one obtains from Eq. 18 the following radial equation:

$$\left(\mathcal{H}_S + \mathcal{H}_{MV} + \mathcal{H}_D + \mathcal{H}_{SO}\right) P_{n\kappa}(r) = \epsilon_{n\kappa} P_{n\kappa}(r) \ . \tag{30}$$

The nonrelativistic Schrödinger Hamiltonian

$$h_S(i) \ = \ -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \tag{31}$$

is augmented by three energy-dependent relativistic terms, i.e., a mass-velocity (MV), a Darwin (D) and a spin-orbit (SO) term

$$\mathcal{H}_{MV} = -\frac{\alpha^2}{2}[\epsilon_{n\kappa} - V(r)]^2 \ , \qquad \mathcal{H}_D = -\frac{\alpha^2}{4}\frac{dV}{dr} B_{n\kappa}(\frac{d}{dr} - \frac{1}{r}), \tag{32}$$

$$\mathcal{H}_{SO} = -\frac{\alpha^2}{4}\frac{dV}{dr} B_{n\kappa}\frac{\kappa+1}{r}, \qquad B_{n\kappa} = \left(1 + \frac{\alpha^2}{2}[\epsilon_{n\kappa} - V(r)]\right)^{-1} \ .$$

In the many-electron case the correct nonlocal Hartree-Fock potential is used in Eq. 30, but a local approximation to it in Eqs. 32. In the CG-AIMP approach the mass-velocity and Darwin operators are cast together with the exchange terms into their spectral representation Eq. 27. The valence orbital energies $\epsilon_{n\kappa}$ are kept fixed during the extraction process and are also used for any semi-core orbitals of the same κ, which are included in the AIMP valence space. A similar strategy is followed in order to deal with the first derivative of the valence orbital in the Darwin term. It should be noted, however, that due to the use of relativistic core orbitals

and core orbital energies relativistic contributions are also present in the Coulomb and shift terms of the AIMP. The WB-AIMP method adds to this a representation of the spin-orbit operator in the form

$$\Delta V^{\lambda}_{cv,so}(i) = \sum_{l}(\sum_{k} \frac{B^{\lambda}_{lk}}{r^{2}_{\lambda i}} e^{-\beta^{\lambda}_{lk} r^{2}_{\lambda i}}) \mathcal{P}^{\lambda}_{l}(i) \vec{l}_{\lambda i} \vec{s}_{i} \mathcal{P}^{\lambda}_{l}(i) \ , \tag{33}$$

where $\vec{l}_{\lambda i} = \vec{r}_{\lambda i} \times \vec{p}_{i}$ and $\vec{s}_{i}$ denote the operators of orbital angular momentum and spin, respectively, and $\mathcal{P}^{\lambda}_{l}$ is the projection operator onto the subspace of angular quantum number l with respect to core λ. The coefficients B^{λ}_{lk} and exponents β^{λ}_{lk} are determined by means of a least-squares fit to the radial components of the Wood-Boring spin-orbit term. We note here in passing, that the Hamiltonian proposed by Cowan and Griffin is not identical to the spin-orbit averaged form of the Hamiltonian proposed by Wood and Boring [90]. The one-component Cowan-Griffin equation is identical to the Wood-Boring equation for $l = 0$, but it yields the eigenvalues of the Klein-Gordon equation (valid for a spin-0 particle) for $l \rangle 0$. The reason is that in addition to the spin-orbit term the Darwin term was also neglected for $l \rangle 0$ by Cowan and Griffin. The CG-AIMP approach, however, uses in fact the properly spin-averaged Wood-Boring Hamiltonian and not the Cowan-Griffin Hamiltonian. Ab initio model potential parameters and corresponding basis sets are available on the internet under `http://www.qui.uam.es/Data/AIMPLibs.html` . Since the model potential approach yields valence orbitals which have the same nodal structure as the all-electron orbitals, it is possible to combine the approach with an explicit treatment of relativistic effects in the valence shell, e.g., in the framework of the DKH no-pair Hamiltonian [54,55]. Corresponding ab initio model potential parameters are available on the internet under `http://www.thch.uni-bonn.de/tc/TCB.download.html` .

3.2 Pseudopotentials

The pseudopotential method was first developed by Hellmann [56] and Gombás [57] around 1935. The quantum mechanical foundations of the method have been investigated later by Fényes and Szépfalusy in the framework of Hartree and Hartree-Fock theory, respectively. The approach became more popular after the work of Preuss [58] for molecules and Phillips and Kleinman [59] for solids. Many of the approximations underlying the method were discussed extensively in the literature, e.g., cf. papers of Weeks *et al.*[1] and Dixon and Robertson [3]. However, since the modern pseudopotentials used today have little in common with the formulas one obtains by a strict derivation of the theory, only a rough derivation in the framework of nonrelativistic Hartree-Fock theory is presented in the following.

The space of orthonormal orbitals of a system with a single valence electron outside a closed shell core may be partitioned into a subspace for the doubly occupied core orbitals φ_{c} and a subspace for the singly occupied valence orbital φ_{v}. For the moment the space of the unoccupied virtual orbitals is not considered. The Fock equation for the valence orbital φ_{v}

$$\mathcal{F}_{v}\varphi_{v} = \epsilon_{v}\varphi_{v} + \sum_{c \neq v} \epsilon_{vc}\varphi_{c} \tag{34}$$

($\mathcal{F}_v$ denotes the Fock operator) can be transformed by application of $1 - P_c$ from the left into a pseudo eigenvalue equation

$$(1 - P_c)\mathcal{F}_v\varphi_v = \epsilon_v\varphi_v \ , \tag{35}$$

with the projector P_c on the subspace of the core orbitals

$$P_c = \sum_c |\varphi_c\rangle\langle\varphi_c| \ . \tag{36}$$

Reductions in the basis set used to represent the valence orbital φ_v can be only achieved if by admixture of core orbitals φ_c the radial nodes are eliminated and the shape of the resulting pseudo (p) valence orbital φ_p is as smooth as possible in the core region (pseudoorbital transformation)

$$\varphi_p = N_p(\varphi_v + \sum_{c\neq v} \omega_c\varphi_c) \ . \tag{37}$$

N_p denotes a normalization factor depending on the coefficients ω_c. The original valence orbital with the full nodal structure in terms of the pseudo valence orbital with the simplified nodal structure

$$\varphi_v = (N_p)^{-1}(1 - P_c)\varphi_p \tag{38}$$

may be inserted into the pseudo eigenvalue problem Eq. 35

$$(1 - P_c)\mathcal{F}_v(1 - P_c)\varphi_p = \epsilon_v(1 - P_c)\varphi_p \ . \tag{39}$$

Using the so-called generalized Phillips-Kleinman pseudopotential [1]

$$V^{GPK} = -P_c\mathcal{F}_v - \mathcal{F}_vP_c + P_c\mathcal{F}_vP_c + \epsilon_vP_c \tag{40}$$

one recovers again a pseudo eigenvalue problem for the pseudo valence orbital

$$(\mathcal{F}_v + V^{GPK})\varphi_p = \epsilon_v\varphi_p \ . \tag{41}$$

If one assumes the core orbitals φ_c to be also eigenfunctions of the Fock operator $\mathcal{F}_v$, i.e., $[\mathcal{F}_v, P_c] = 0$, and uses the idempotency of the projection operator $P_c = P_c^n$ ($n \leq 1$), one recovers a simplified pseudo eigenvalue problem

$$(\mathcal{F}_v + V^{PK})\varphi_p = \epsilon_v\varphi_p \tag{42}$$

containing the so-called Phillips-Kleinman pseudopotential [59]

$$V^{PK} = \sum_{c\neq v}(\epsilon_v - \epsilon_c)|\varphi_c\rangle\langle\varphi_c| \ . \tag{43}$$

The transition from a single valence electron to n_v valence electron requires formally in Eq. 39 the following substitutions:

$$\mathcal{F}_v \ \longmapsto \ \sum_i^{n_v} \mathcal{F}_v(i) + \sum_{i\langle j}^{n_v} g(i,j) \ , \qquad \epsilon_v \ \longmapsto \ E^v \ , \tag{44}$$

$$(1 - P_c) \ \longmapsto \ \prod_i^{n_v}(1 - P_c(i)) \ , \qquad \varphi_p \ \longmapsto \ \Psi^p \ .$$

The sum of effective one-particle operators $\mathcal{F}_v(i)$ has to be augmented by the interelectronic interaction terms $g(i,j)$ between the valence electrons. The valence model Hamiltonian $\mathcal{H}_v$ then reads

$$\mathcal{H}_v = \prod_k^{n_v}(1-P_c(k))[\sum_i^{n_v}\mathcal{F}_v(i) + \sum_{i\langle j}^{n_v} g(i,j)]\prod_l^{n_v}(1-P_c(l)) \qquad (45)$$
$$+ E_v[\sum_i^{n_v} P_c(i) - \sum_{i\langle j}^{n_v} P_c(i)P_c(j) - + \ ...] \ + \ V_{cc} \ .$$

This form of valence model Hamiltonian is essentially useless for practical calculations, since it contains complicated many-electron operators due to the introduction of products of projection operators. In addition the use of such a Hamiltonian would not bring about any computational savings with respect to an all-electron treatment, since the derivation given so far essentially consists of a rewriting of the Fock equation for a valence orbital in a different form. Reductions in the computational effort can be only achieved by elimination of the core electron system and simulation of its influence on the valence electrons by introducing a suitable model Hamiltonian:

$$h_v(i) \ = \ [(1-P_c(i))\mathcal{F}_v(i)(1-P_c(i)) + E_v P_c(i)] \ \longmapsto \ -\frac{1}{2}\Delta_i + V_{cv}(i) \ , \qquad (46)$$

$$g_v(i,j) \ = \ [(1-P_c(i))(1-P_c(j))g(i,j)(1-P_c(i))(1-P_c(j))] \ \longmapsto \ \frac{1}{r_{ij}} \ .$$

4 Analytical form of pseudopotentials

The simplest and historically the first choice is the local ansatz for ΔV_{cv}^{λ} in Eq. 22, however, such an ansatz is too inaccurate and therefore has soon been replaced by a so-called semilocal form. In case of quasirelativistic pseudopotentials, i.e., when spin-orbit coupling is included, the semilocal ansatz in two-component form may be written as

$$\Delta V_{cv}^{\lambda}(\vec{r}_{\lambda i}) = \sum_{l=0}^{L-1}\sum_{j=|l-1/2|}^{l+1/2}(V_{lj}^{\lambda}(r_{\lambda i}) - V_L^{\lambda}(r_{\lambda i}))P_{lj}^{\lambda}(i) + V_L^{\lambda}(r_{\lambda i}) \ . \qquad (47)$$

P_{lj}^{λ} denotes a projection operator on spinor spherical harmonics centered at the core λ

$$P_{lj}^{\lambda}(i) = P_{l,l\pm1/2}^{\lambda}(i) = P_{\kappa}^{\lambda}(i) = \sum_{m_j=-j}^{j} \mid \lambda l j m_j(i)\rangle\langle\lambda l j m_j(i) \mid \ . \qquad (48)$$

For scalar-quasirelativistic calculations, i.e., when spin-orbit coupling is neglected, a one-component form may be obtained by averaging over the spin

$$\Delta V_{cv,av}^{\lambda}(\vec{r}_{\lambda i}) = \sum_{l=0}^{L-1}(V_l^{\lambda}(r_{\lambda i}) - V_L^{\lambda}(r_{\lambda i}))P_l^{\lambda}(i) + V_L^{\lambda}(r_{\lambda i}) \ . \qquad (49)$$

The projection operator P_l^λ refers now to the spherical harmonics centered at the core λ

$$P_l^\lambda(i) = \sum_{m_l=-l}^{l} \mid \lambda l m_l(i)\rangle\langle \lambda l m_l(i) \mid \ . \tag{50}$$

A spin-orbit operator may be defined

$$\Delta V_{cv,so}^\lambda(\vec{r}_{\lambda i}) = \sum_{l=1}^{L-1} \frac{\Delta V_l^\lambda(r_{\lambda i})}{2l+1}[l P_{l,l+1/2}^\lambda(i) - (l+1)P_{l,l-1/2}^\lambda(i)] \tag{51}$$

which contains essentially the difference between the two-component pseudopotentials

$$\Delta V_l^\lambda(r_{\lambda i}) = V_{l,l+1/2}^\lambda(r_{\lambda i}) - V_{l,l-1/2}^\lambda(r_{\lambda i}) \ . \tag{52}$$

For practical calculations it is advantageous to separate space and spin

$$\Delta V_{cv,so}^\lambda(\vec{r}_{\lambda i}) = \sum_{l=1}^{L-1} \frac{2\Delta V_l^\lambda(r_{\lambda i})}{2l+1} P_l^\lambda(i)\vec{l}_{\lambda i}\vec{s}_i P_l^\lambda(i) \ . \tag{53}$$

The potentials V_{lj}^λ and V_l^λ ($l = 0$ to $l = L$) respectively ΔV_l^λ ($l = 1$ to $l = L$ -1) are represented as a linear combination of Gaussians multiplied by powers of the electron-core distance:

$$V_{lj}^\lambda(r_{\lambda i}) = \sum_k A_{ljk}^\lambda \ r_{\lambda i}^{n_{ljk}^\lambda} \ exp(-a_{ljk}^\lambda r_{\lambda i}^2) \ , \tag{54}$$

$$[\Delta]V_l^\lambda(r_{\lambda i}) = \sum_k [\Delta]A_{lk}^\lambda \ r_{\lambda i}^{n_{lk}^\lambda} \ exp(-a_{lk}^\lambda r_{\lambda i}^2) \ . \tag{55}$$

The necessary one-electron integrals over cartesian Gaussians have been presented, e.g., by McMurchie and Davidson [60] or by Pitzer and Winter [61,62]. Alternatively, making use of the operator identity

$$\sum_{m_l=-l}^{+l} |lm_l\rangle V_l(r)\langle lm_l| = \sum_{i,j} |\chi_i^{(l)}\rangle A_{ij}^{(l)} \langle \chi_j^{(l)}| \ . \tag{56}$$

a nonlocal representation in a (nearly) complete auxiliary basis set can be used instead [63]. Once the constants $A_{ij}^{(l)}$ have been determined the integral evaluation is reduced to overlap integrals (between the auxiliary basis and the actual molecular basis sets) and therefore the derivatives with respect to the nuclear coordinates needed in geometry optimizations become much easier to evaluate.

In case of large cores a correction to the point charge repulsion model in Eq. 24 is needed. A Born-Mayer type ansatz proved to be quite successful

$$\Delta V_{cc}^{\lambda\mu}(r_{\lambda\mu}) = B_{\lambda\mu} exp(-b_{\lambda\mu} r_{\lambda\mu}) \ . \tag{57}$$

For a core-nucleus repulsion the parameters $B_{\lambda\mu}$ and $b_{\lambda\mu}$ can be obtained directly from the electrostatic potential of the atomic core electron system, for a core-core repulsion the deviation from the point charge model has to be determined

by Hartree-Fock or Dirac-Hartree-Fock calculations for the interaction between the frozen cores.

Relativistic pseudopotentials to be used in four-component Dirac-Hartree-Fock calculations can also be successfully generated and used [64], however, the advantage of obtaining accurate results at a low computational cost is certainly lost within this scheme.

5 Adjustment of pseudopotentials

5.1 Shape-consistent pseudopotentials

The origin of shape-consistent pseudopotentials [65,66] lies in the insight that the admixture of only core orbitals to valence orbitals in order to remove the radial nodes leads to too contracted pseudo valence orbitals and finally as a consequence to poor molecular results, e.g., to too short bond distances. It has been recognized about 20 years ago that it is indispensable to have the same shape of the pseudo valence orbital and the original valence orbital in the spatial valence region, where chemical bonding occurs. Formally this requires also an admixture of virtual orbitals in Eq. 37. Since these are usually not obtained in finite difference atomic calculations, another approach was developed. Starting point is an atomic all-electron calculation at the nonrelativistic, scalar-relativistic or quasirelativistic Hartree-Fock or the Dirac-Hartree-Fock level. In the latter case the small components are discarded and the large components of the energetically lowest valence shell of each quantum number lj are considered as valence orbitals after renormalization. To generate the pseudo valence orbitals $\varphi_{p,lj}$ the original valence orbitals $\varphi_{v,lj}$ are kept unchanged outside a certain matching radius r_c separating the spatial core and valence regions (shape-consistency; exactly achieved only for the reference state), whereas inside the matching radius the nodal structure is discarded and replaced by a smooth and in the interval [0,r_c] nodeless polynomial expansion $f_{lj}(r)$:

$$\varphi_{v,lj}(r) \rightarrow \varphi_{p,lj}(r) = \begin{cases} \varphi_{v,lj}(r) \text{ for } r \geq r_c \\ f_{lj}(r) \text{ for } r \langle r_c \end{cases} \tag{58}$$

The free parameters in f_{lj} are determined by normalization and continuity conditions, e.g., matching of f_{lj} and $\varphi_{v,lj}$ as well as their derivatives at r_c. The choice of r_c as well as the choice of f_{lj} is in certain limits arbitrary and a matter of experience.

Having a nodeless and smooth pseudo valence orbital $\varphi_{p,lj}$ and the corresponding orbital energy $\epsilon_{v,lj}$ at hand, the corresponding radial Fock equation

$$(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{lj}^{PP}(r) + W_{p,lj}[\{\varphi_{p',l'j'}\}])\varphi_{p,lj}(r) = \epsilon_{v,lj}\varphi_{p,lj}(r) \tag{59}$$

can be solved pointwise for the unknown pseudopotential V_{lj}^{PP} for each combination lj of interest. In Eq. 59 the term $W_{p,lj}$ stands for an effective valence Coulomb and exchange potential for $\varphi_{p,lj}$. Relativistic effects enter the potentials implicitly via the value of the orbital energy $\epsilon_{v,lj}$ and the shape of the pseudo valence orbital outside the matching radius. The resulting potentials V_{lj}^{PP} are tabulated on a grid

and are usually fitted to a linear combination of Gaussian functions according to

$$V^{PP} = -\frac{Q}{r} + \sum_{lj}(\sum_{k} A_{lj,k} r^{n_{lj,k}-2} e^{-\alpha_{lj,k} r^2})\mathcal{P}_{lj} \ . \tag{60}$$

Shape-consistent pseudopotentials including spin-orbit operators based on Dirac-Hartree-Fock calculations using the Dirac-Coulomb Hamiltonian have been generated by Christiansen, Ermler and coworkers [67,68,69,70,71,72,73,74,75,76]. The potentials and corresponding valence basis sets are available on the internet under `http://www.clarkson.edu/~pac/reps.html` . A similar set for main group and transition elements based on scalar-relativistic Cowan-Griffin all-electron calculations was published by Hay and Wadt [77,78,79,80,81]. Another almost complete set of pseudopotentials has been published by Stevens and coworkers [82,83,84].

5.2 Energy-consistent pseudopotentials

Energy-consistent ab initio pseudopotentials developed from energy-adjusted semiempirical pseudopotentials, i.e., potentials which were fitted to reproduce the experimental atomic spectrum. Due to the problems to account accurately for valence correlation effects, such semiempirical energy-adjustment could only be performed successfully for one-valence electron systems. The results for alkaline and alkaline-earth systems were quite good, however, due to the limited validity of the frozen-core approximation when going from a highly charged one-valence electron ion to a neutral atom or nearly neutral ion, it essentially failed for other elements, especially transition metals. However, the idea to fit exclusively to quantum mechanical observables like total valence energies (note that these may be written as sums of ionization potentials and excitation energies) instead of to rely on quantities like orbitals and orbital energies only meaningful in an approximate one-particle picture is very appealing and the approach regained attention in the ab initio framework [85].

In the most recent version of the energy-consistent pseudopotential approach the reference data is derived from finite-difference all-electron multi-configuration Dirac-Hartree-Fock calculations based on the Dirac-Coulomb or Dirac-Coulomb-Breit Hamiltonian [86]. These calculations are performed for a multitude of electronic configurations/states/levels I of the neutral atom and the low-charged ions. The total valence energies E_I^{AE} derived from these calculations define the pseudopotential parameters for a given ansatz in a least-squares sense. A corresponding set of finite-difference valence-only calculations (especially the same coupling scheme and correlation treatment has to be applied) is performed to generate the total valence energies E_I^{PP}, and the parameters are varied in such a way that the sum of weighted squared errors in the total valence energies becomes a minimum, i.e.,

$$\sum_{I}(w_I[E_I^{PP} - E_I^{AE}]^2) := min \ . \tag{61}$$

In principle this formalism can be used to generate one-, two- and also four-component pseudopotentials at any desired level of relativity (nonrelativistic Schrödinger, or relativistic Wood-Boring, Douglas-Kroll-Hess, Dirac-Coulomb or

Dirac-Coulomb-Breit Hamiltonian; implicit or explicit treatment of relativity in the valence shell) and electron correlation (single- or multi-configurational wavefunctions, e.g., the use of an intermediate coupling scheme is possible). The pseudo valence orbitals usually agree very well with the all-electron orbitals in the valence region, cf., e.g., Fig. 6. Parameters of energy-consistent ab initio pseudopo-

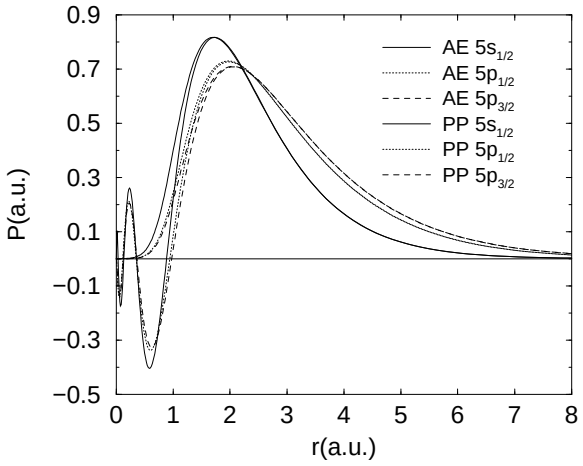

Figure 6. Valence spinors of the iodine atom in the $[_{46}\mathrm{Pd}]\ 5s^2\ 5p^5$ ground state configuration from average-level all-electron (AE) multiconfiguration Dirac-Hartree-Fock calculations and corresponding valence-only calculations using a relativistic energy-consistent 7-valence-electron pseudopotential (PP).

tentials and corresponding valence basis sets have been presented for almost all elements of the periodic table by Dolg, Preuss, Schwerdtfeger, Stoll and coworkers [85,86,87,88,89,90,91,92,93,94,95,96,97]. They are also available on the internet under `http://www.theochem.uni-stuttgart.de` . Since the functional form of energy-consistent pseudopotentials is identical to the one of shape-consistent pseudopotentials, both types of pseudopotentials can be used in standard quantum chemical program packages (COLUMBUS, GAUSSIAN, GAMESS, MOLPRO, TURBOMOLE, ...) as well as polymer or solid state codes using Gaussian basis sets (CRYSTAL, WANNIER, ...).

5.3 Limitations of accuracy

Effective core potentials are usually derived for atomic systems at the finite difference level and used in subsequent molecular calculations using finite basis sets. They are designed to model the more accurate all-electron calculations at low cost, but without significant loss of accuracy. Unfortunately the correct relativistic all-electron Hamiltonian for a many-electron system is not known and the various pseudopotentials merely model the existing approximate formulations. For most cases of chemical interest, e.g., geometries and binding energies, it usually does not

matter which particular Hamiltonian model is used, i.e., typically errors due to the finite basis set expansion or the limited correlation treatment are much larger than the small differences between the various all-electron models. For very accurate cal-

Table 1. Relative average energy of a configuration of Hg from all-electron (AE) multi-configuration Dirac-Hartree-Fock (DHF) average level calculations using the Dirac-Coulomb (DC) Hamiltonian with a finite nucleus with Fermi charge distribution (fn) or a point nucleus (pn). Contributions from the frequency-dependent Breit (B) interaction (frequency of the exchanged photon 10^3 cm^{-1}) and estimated contributions from quantum electrodynamics (QED, i.e., self-interaction and vacuum polarization) were evaluated in first-order perturbation theory. Errors of energy-consistent pseudopotentials (PP) with 20 valence electrons and different numbers of adjustable parameters with respect to the AE DHF(DC,pn)+B+QED data. All values in cm^{-1}.

configuration		AE, DHF (DC)+B+QED		contribution		error	
		fn	pn	B	QED	PP[a]	PP[b]
Hg	$6s^2$	0	0	0.0	0.0	0.0	0.0
	$6s^1\ 6p^1$	35632.3	35674.4	-52.5	-18.7	1.3	0.0
Hg^+	$6s^1$	68842.1	68885.1	-98.6	-11.6	-0.1	0.0
	$7s^1$	154127.4	154206.2	-220.6	-42.4	-0.4	0.0
	$8s^1$	178127.5	178215.5	-238.4	-41.7	1.1	0.1
	$9s^1$	188751.0	188843.2	-244.1	-40.6	1.6	-0.1
	$6p^1$	122036.8	122128.9	-154.2	-41.8	0.6	0.0
	$7p^1$	167514.3	167609.2	-224.1	-40.3	-3.3	0.0
	$8p^1$	183808.0	183903.6	-238.5	-40.0	-0.8	0.0
	$9p^1$	191697.2	191793.1	-244.0	-39.6	0.6	0.0
Hg^{++}		206962.2	207058.4	-249.8	-39.5	2.6	0.0

[a] energy-consistent pseudopotential with 26 adjustable parameters.

[b] energy-consistent pseudopotential with 54 adjustable parameters.

culations of excitation energies, ionization potentials and electron affinities, or for a detailed investigation of errors inherent in the effective core potential approach, however, such differences might become important. Tables 1 and 2 demonstrate that for very special cases like Hg, with a closed $5d^{10}$-shell in all electronic states considered, a small-core energy-consistent pseudopotential using a semilocal ansatz reaches an accuracy of 10 cm^{-1}, which is well below the effects of the nuclear model, the Breit interaction or higher-order quantum electrodynamical contributions. We also note that differences between results obtained with a frequency-dependent Breit term and the corresponding low-frequency limit amount to up to 10 cm^{-1}. Moreover, the quantum electrodynamic corrections listed in tables 1 and 2 might change by up to 20 cm^{-1} when more recent methods of their estimation are applied [98,99]. Therefore, it is important to state exactly which relativistic all-electron model the effective core potential simulates and, when comparing effective core potentials of different origins, to separate differences in the underlying all-electron approach from errors in the potential itself, e.g., due to the size of the core, the method of adjustment or the form of the valence model Hamiltonian. In this context we want to point out that the seemingly large errors for energy-adjusted pseudopotentials

reported by Mosyagin *et al.* [100,101] are mainly due to the invalid comparison of Wood-Boring-energy-adjusted and Dirac-Fock-orbital-adjusted pseudopotentials to all-electron Dirac-Fock data, i.e., differences in the all-electron model are considered to be pseudopotential errors.

Note that in the above example of Hg the average energy of a configuration (table 1) and the fine-structure (table 2) of one-valence electron states is more accurately represented than the fine-structure of the $6s^1$ $6p^1$ configuration. The small errors in the latter case are a consequence of the pseudoorbital transformation and the overestimation of the 6s-6p exchange integral with pseudo-valence spinors. This error could be reduced further upon using a smaller core, but the efficiency of the approach would be sacrificed. It is also obvious from the compiled data that the accuracy of the valence model Hamiltonian is also a question of the number of adjustable parameters. Claims that such very high accuracy as demonstrated here can only be achieved by adding nonlocal terms for outer core orbitals to the usual semilocal terms [100,101] appear to be invalid, at least for energy-consistent pseudopotentials. Moreover, additional nonlocal terms obviously do not improve the performance for atomic states with a $5d^9$ occupation or in molecular calculations (cf., e.g., tables III and XVII in Mosyagin *et al.* [100]).

Table 2. As table 1, but for fine-structure splittings. All values in cm^{-1}.

configuration		splitting	AE,DHF (DC)+B+QED		contribution		error	
			fn	pn	B	QED	PP[a]	PP[b]
Hg	$6s^16p^1$	$^3P_1$-$^3P_0$	1987.7	1988.6	-25.5	0.9	-14.7	3.0
		$^3P_2$-$^3P_0$	6082.6	6084.8	-96.8	2.9	-28.3	-3.5
		$^1P_1$-$^3P_0$	22994.4	22982.3	-72.4	2.2	-12.4	-9.4
Hg^+	$6p^1$	$^2P_{3/2}$-$^2P_{1/2}$	7765.3	7768.8	-132.8	4.8	-14.8	-0.1
	$7p^1$	$^2P_{3/2}$-$^2P_{1/2}$	2136.8	2137.9	-29.0	1.1	-1.7	0.2
	$8p^1$	$^2P_{3/2}$-$^2P_{1/2}$	939.4	939.9	-12.1	0.4	-4.6	-0.3
	$9p^1$	$^2P_{3/2}$-$^2P_{1/2}$	498.7	498.9	-6.2	0.2	-3.5	0.0

[a] energy-consistent pseudopotential with 26 adjustable parameters.

[b] energy-consistent pseudopotential with 54 adjustable parameters.

6 Core Polarization Potentials

The frozen-core approximation is underlying the effective core potential schemes. One may ask if it is possible to account for static (polarization of the core at the Hartree-Fock level) and dynamic (core-valence correlation) polarization of the cores in a both efficient and accurate way. The core polarization potential (CPP) approach originally developed by Meyer and coworkers [102] for all-electron calculations and adapted by the Stuttgart group [103] for pseudopotential calculations proved to be quite successful in the past. The core polarization potential is written in the

following form

$$V_{cpp} = -\frac{1}{2}\sum_{\lambda}\alpha_\lambda \vec{f_\lambda}^2 + \sum_{\lambda,i} V^\lambda(i) \ . \tag{62}$$

Here α_λ denotes the dipole polarizability of the core λ and $\vec{f_\lambda}$ is the electric field at core λ generated by all other cores and nuclei as well as all valence electrons. Since the validity of the underlying multipole expansion breaks down for small distances from the core λ, the field has to be multiplied by a cut-off function:

$$\vec{f_\lambda} = -\sum_i \frac{\vec{r}_{i\lambda}}{r^3_{i\lambda}}(1 - exp(-\delta^\lambda_e r^2_{i\lambda}))^{n_e} + \sum_{\mu\neq\lambda} Q_\mu \frac{\vec{r}_{\mu\lambda}}{r^3_{\mu\lambda}}(1 - exp(-\delta^\lambda_c r^2_{\mu\lambda}))^{n_c} \ . \tag{63}$$

The necessary integrals over cartesian Gaussian functions have been presented by Schwerdtfeger and Silberbach [104]. In those cases where ns and np valence orbitals are present together with (n-1)d and (n-2)f valence orbitals, e.g., for Cs, it proved to be more accurate to augment the core polarization potential by a short-range local potential [64]

$$V^\lambda(i) = C^\lambda exp(-\gamma^\lambda r^2_{i\lambda}) \ . \tag{64}$$

A l-dependent cut-off function in Eq. 63 might even be more accurate [105].

7 Calibration Studies

Calibration studies, especially on molecules, are very important for effective core potential methods. Excellent results in atomic calculations are a necessary prerequisite for successful molecular calculations, but provide no guarantee for them. Therefore, effective core potentials should be systematically tested on atoms and small molecules before using them in larger systems. This is especially necessary for cases where a large core is used for economical reasons.

A number of such molecular calibration studies has been performed in the past for energy-consistent pseudopotentials [106,107,108,109,110,111]. Comparison is made to experimental data and/or all-electron results. Some care has to be taken before drawing final conclusions on the quality of pseudopotentials. Usually all molecular calculations are performed using finite basis sets, both at the one-electron and the many-electron level. The truncation of these basis sets leads to errors both at the all-electron and at the pseudopotential level. Most of the time it is relatively easy to generate basis sets of nearly the same quality at the one-particle level, e.g., by augmenting the standard all-electron and pseudopotential basis sets (which of course have to be of the same quality for the valence shells) by the same polarization and correlation functions. It is recommended, however, to approach the basis set limit, at least up to a given angular quantum number, as closely as possible. At the many-particle level it is sometimes more difficult to come to directly comparable basis sets. As an example imagine a large-core pseudopotential augmented by a core polarization potential, which both accounts for static and dynamic core polarization. Static core polarization occurs in the all-electron calculations automatically at the self-consistent field level and can be accounted for in the frozen-core case by single excitations out of the spherical core. Comparing the results of such all-electron

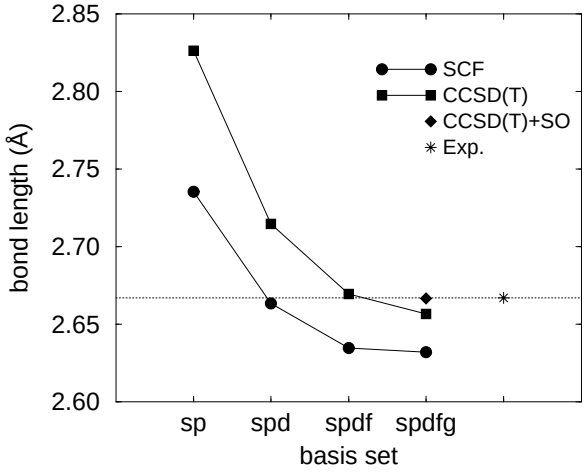

Figure 7. Bond length of the iodine dimer I_2 depending on the basis set. A subset of a 25s21p14d4f3g basis set and a relativistic energy-consistent 7-valence electron pseudopotential augmented by a core polarization potential is used. The experimental value is indicated by a vertical dashed line. The scalar-quasirelativistic pseudopotential calculations at the Hartree-Fock self-consistent field (SCF) and coupled-cluster with single, double and perturbative triple excitations (CCSD(T)) level of theory use an uncontracted (25s21p14d4f3g) Gaussian type basis set. Spin-orbit corrections (+SO) were derived from limited two-component configuration interaction calculations using the quasirelativistic pseudopotential and a contracted [3s3p1d1f] valence basis set of polarized triple-zeta quality.

calculations to pseudopotential Hartree-Fock calculations including the core polarization potential is not entirely correct, however, since the latter also accounts for core-valence correlation. This effect can be modelled in all-electron calculations by single excitations out of the spherical core and simultaneous single excitations in the valence shell. Thus, comparing the results of an all-electron calculation where all electrons are correlated to a correlated pseudopotential calculation with a core polarization potential is also not entirely correct, since the former calculation also accounts for core-core correlation effects. In addition, attention has to be paid with respect to the relativistic contributions taken into account in the Hamiltonian, i.e., the relativistic scheme used in the all-electron reference calculations should not be different, e.g., more approximate, from the scheme used to obtain the reference data in the pseudopotential generation. As an example for a calibration study the results for the iodine dimer I_2 in its ground state are compared to Hartree-Fock and coupled-cluster calculations using a relativistic energy-consistent 7-valence electron pseudopotential together with an uncontracted (25s21p14d4f3g) basis set. The pseudopotential was augmented by a core polarization potential. The results for the bond length, binding energy and vibrational frequency in dependence on the highest angular quantum number used in the basis set are given in Figs. 7 to 9. It is clear from these graphs that the experimental values are only approached for a large basis set and after inclusion of spin-orbit effects. It should be mentioned here that the core polarization potential also makes significant contributions, e.g., -0.03

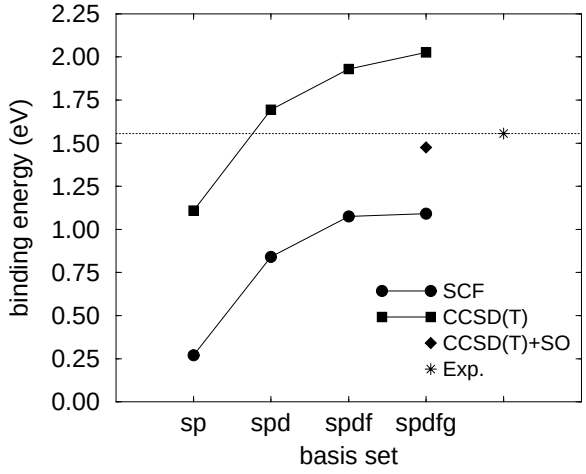

Figure 8. As figure 7, but for the binding energy.

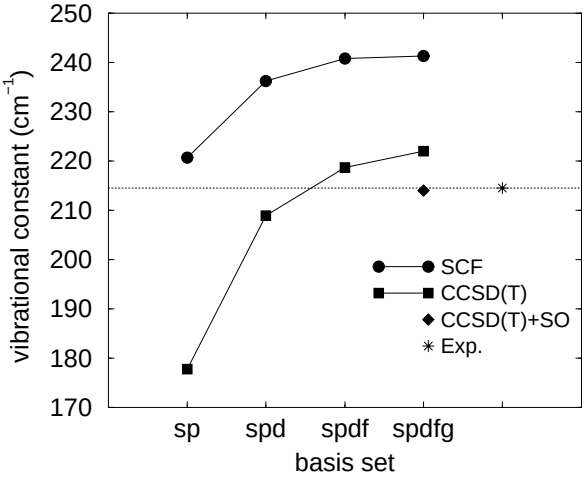

Figure 9. As figure 7, but for the vibrational constant.

Å, +0.09 eV and +3 cm^{-1} for the bond length, binding energy and vibrational constant, respectively, at the Hartree-Fock level. The performance of energy-consistent quasirelativistic 7-valence electron pseudopotentials for all halogen elements has been investigated in a study of the monohydrides and homonuclear dimers [112]. Special attention was also paid to the accuracy of valence correlation energies obtained with pseudo valence orbitals [113,114]. Some of the results for the dimers is presented in tables 3 to 5. The applied basis sets were uncontracted all-electron basis sets: (15s9p5d4f3g) for fluorine, (21s13p5d4f3g) for chlorine, (22s17p11d4f3g)

Table 3. Bond lengths R_e (Å) of the homonuclear halogen dimers from all-electron (AE) Douglas-Kroll-Heß (DKH) and valence-only pseudopotential (PP) Hartree-Fock self-consistent field (SCF) calculations. Core-valence correlation and valence correlation are accounted for by a core polarization potential (CPP) and a coupled-cluster treatment with singles, doubles and perturbative triples (CCSD(T)) including spin-orbit corrections (+SO). For the basis sets cf. the text.

	F_2	Cl_2	Br_2	I_2	At_2
AE DKH,SCF	1.327	1.975	2.273	2.671	2.843
PP,SCF	1.324	1.964	2.266	2.669	2.861
PP+CPP,SCF	1.323	1.958	2.252	2.639	2.822
PP+CPP,CCSD(T)+SO	1.409	1.982	2.281	2.668	2.979
Exp.	1.412	1.988	2.281	2.666	

Table 4. As table 3, but for vibrational constants ω_e (cm^{-1}).

	F_2	Cl_2	Br_2	I_2	At_2
AE DKH,SCF	1267[a]	615	354	232	169
PP,SCF	1271	619	356	238	168
PP+CPP,SCF	1273	622	359	241	172
PP+CPP,CCSD(T)+SO	927	561	324	215	117
Exp.	917	560	325	215	

[a] nonrelativistic result.

Table 5. As table 3, but for binding energies D_e (eV).

	F_2	Cl_2	Br_2	I_2	At_2
AE DKH,SCF	-1.07	1.23	1.01	0.92	0.81
PP,SCF	-1.03	1.26	1.04	0.95	0.79
PP+CPP,SCF	-1.03	1.27	1.08	1.04	0.95
PP+CPP,CCSD(T)+SO	1.66	2.44	1.95	1.57	0.80
Exp.	1.66	2.51	1.99	1.56	

for bromine, (25s20p14d4f3g) for iodine, and (27s22p19d13f3g) for astatine. At the HF level the calibration for the scalar-quasirelativistic pseudopotentials was against all-electron calculations using the Douglas-Kroll-Heß Hamiltonian, whereas at the CCSD(T) level including spin-orbit corrections from limited two-component CI calculations the calibration was with respect to experimental data.

A typical example demonstrating that pseudopotentials account for the major relativistic effects quite accurately and the largest errors in practical calculations are actually due to finite basis sets and too limited correlation treatments is provided by a series of theoretical investigations of gold monofluoride AuF (cf. table 6). All calculations used the same scalar-relativistic energy-consistent 19-valence-electron pseudopotential for Au [115], but the quality of the valence-only calculations was systematically increased during the years. Originally it was believed that AuF is not a stable molecule, until its existence was first predicted theoretically [115,116]

Table 6. Bond length R_e (Å), binding energy D_e (eV) and vibrational constant ω_e (cm^{-1}) of gold monofluoride AuF in the $^1\Sigma^+$ ground state. All theoretical results have been obtained with a 19-valence-electron energy-consistent pseudopotential adjusted to multi-configuration Dirac-Hartree-Fock reference data [115] using different basis sets and valence correlation methods.

method	basis	year	R_e	D_e	ω_e
CISD+SCC(LD)[115]	A	1989	1.978	2.24	509
CEPA-1[115]	A	1989	1.991	2.52	488
Exp.[117]		1992			560
QCISD(T)[116]	B	1994	1.939	3.09	539
Exp.[118]		1994		3.2	
CCSD(T)[119]	C	1997	1.909	3.29	573
MRCI+SCC(S)[119]	C	1997	1.916	3.14	562
MRACPF[119]	C	1997	1.916	3.20	560

Basis sets: A: Au (8s6p5d1f)/[7s3p4d1f], F (13s8p1d)/[7s3p1d];
B: Au (10s8p7d1f)/[9s5p6d1f], F (15s10p2d1f)/[9s7p2d1f];
C: Au (10s8p7d4f2g)/[9s5p6d4f2g], F (13s7p4d3f2g)/[6s5p4d3f2g] (aug-cc-p-vqz).

and later also proven experimentally [117,118]. The most recent calculations [119] are in excellent agreement with the available experimental data.

8 A few hints for practical calculations

Some of the simple hints for practical applications of effective core potentials given in the following may appear to be trivial or superfluous for some of the readers, but experience during the last years showed that they may be welcome by the more application-oriented ones who are less familiar with the methods.

Effective core potentials are usually a good and safe choice when properties related to the valence electron system are to be investigated. It should always be remembered, however, that the size of the core not only determines the computational effort, but it also influences the accuracy of the results. Small-core and medium-core potentials are usually safe to use, whereas the range of large-core potentials is much more limited. In the latter case it might be important to include a core-core and/or core-nucleus repulsion correction as well as a core polarization potential. It is not a wise decision to simply neglect these terms, e.g., because the CPP is not implemented in GAUSSIAN yet.

When using an effective core potential for the first time always do an atomic test calculation first, e.g., for the ionization potential or electron affinity, in order to check the correctness of your input and/or the programs library data. Especially in pseudopotential calculations well-known sources of input errors are the $1/r^n$ prefactors used in some parametrizations or the presence/absence of a local potential. It is recommended to use the valence basis set coming with the effective core potential, possibly augmented by additional diffuse and polarizations functions. Especially in case of pseudopotentials, where the detailed innermost shape of the pseudoorbitals is essentially arbitrary, it is not recommended to use (contracted) all-electron basis

sets or valence basis sets from other potentials, since significant basis set superposition errors may result. However, the added diffuse and polarization functions may safely be taken from all-electron or other effective core potential basis sets.

When comparing to other all-electron or valence-only calculations use basis sets and correlation treatments of the same quality and make sure that relativistic effects are included at similar levels. Note that in all-electron calculations basis set superposition errors tend to be larger than in valence-only calculations.

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